generated for reaction to occur. This explains why the reaction slows markedly as the temperature is lowered. A point raised by this data is "What is the intimate mechanism of superoxide generation?"; does it, for example, involve formation of a transient oxygen adduct that immediately eliminates superoxide? The reciprocal base dependence of the autoxidation kinetics is most easily interpreted in these terms; however, there are many literature discussions that argue strongly against mechanisms wherein free superoxide is eliminated from an oxygen adduct in aprotic solvents for thermodynamic reasons.[24] If this is not the mechanism in our example, how does one then explain the inverse base dependence of the kinetics? One plausible explanation arises from the electrochemical data discussed earlier. We described experiments wherein the addition of increasing amounts of pyridine to one of our iron(II) complexes in DMF leads to a 115 mV positive shift in the metal(II/III) couple. This shift, which makes the metal harder to oxidize, might therefore explain the observed inverse base dependence of the kinetics of autoxidation if the reaction proceeds via our outer-sphere oxidation. As the base concentration increases, the metal gets harder to oxidize and the outer-sphere oxidation reaction slows down. That superoxide ion can be generated in aprotic solvents by outer-sphere oxidation of metal ions by O_2 is well-documented,[24] and so this may represent the most realistic intimate mechanism for reaction 6.

Individual components of the overall reaction scheme presented in eq 5–10 have a number of precedents. In particular, reduction reaction 6 is essentially that observed in porphyrin systems when KO_2 reacts with iron(III).[25] Reaction 10 is also observed in Fenton type chemistry of iron(III) and peroxide.[26] The scheme presented therefore represents a system in which individual, previously noted reactions have combined to produce a deceptively reversible reaction between dioxygen and iron(II) species.

Dioxygen adduct formation by metal atoms in coordination compounds has long been a matter of fundamental interest. Growing activity in application areas assures that their interest will continue. Perhaps the example shown here of a process that superficially appears to involve such an oxygen complex but, in fact, does not will provide some guidance in the clarification of other questionable systems.

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Registry No. I (R^1 = *m*-xylene, R^2 = H, R^3 = CH_3, M = Fe^{II}–py), 85166-57-0; I (R^1 = $(CH_2)_2$, R^2 = H, R^3 = CH_3, M = Fe^{II}–py), 85166-61-6; I (R^1 = $(CH_2)_3$, R^2 = H, R^3 = CH_3, M = Fe^{II}–py), 85166-65-0; I (R^1 = $(CH_2)_4$, R^2 = H, R^3 = CH_3, M = Fe^{II}–py), 85166-67-2; I (R^1 = 9,9-bis(3-propyl)fluorene, R^2 = H, R^3 = CH_3, M = Fe^{II}-py), 85166-69-4; I (R^1 = $(CH_2)_3$, R^2 = H, R^3 = CH_3, M = py-Fe^{II}-CO), 85166-71-8; I (R^1 = *m*–xylene, R^2 = H, R^3 = CH_3, M = py-$Fe^{III}OH_2$, 85185-08-6; $[H_8((m\text{-xylyl})(NHEthi)_2Me_2[16]\text{-}tetraeneN_4)_2](ZrCl_4)_4$, 85166-59-2; $Fe^{II}(py)_4Cl_2$, 15138-92-8; $[H_2((CH_2)_2(NHEthi)_2Me_2[16]tetraeneN_4)_2](PF_6)_2$, 85166-63-8; $Fe^{II}(py)_2Cl_2$, 15616-26-9; O_2, 7782-44-7; CO, 630-08-0.

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Sulfinylaniline Complexes of Iron(0)

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A number of synthetic routes have been utilized to prepare a series of $[Fe(PR_3)_2(CO)_2(ArNSO)]$ derivatives (I) (R = $PhCH_2$, 4-$MeOC_6H_4$, 4-MeC_6H_4, Ph, 4-ClC_6H_4; Ar = 4-$MeOC_6H_4$, 4-MeC_6H_4, 4-FC_6H_4, Ph, 4-ClC_6H_4, 4-BrC_6H_4, 4-$NO_2C_6H_4$). The most useful was the reaction of $[Fe_2(CO)_9]$ with PR_3 and ArNSO in tetrahydrofuran at 20 °C, but its efficacy depended on both PR_3 and Ar. In the absence of PR_3, this reaction gave red oils tentatively formulated as $[Fe(CO)_4(\eta^1\text{-}(N)\text{-}ArNSO)]$, which with PR_3 rapidly form I. Trialkyl phosphite and alkyl isocyanide nucleophiles displace PPh_3 and/or CO from I with the formation of, e.g., $[Fe(PPh_3)(P(OCH_2)_3CMe)(CO)_2(PhNSO)]$, $[Fe(P(OMe)_3)_2(CO)_2(4\text{-}NO_2C_6H_4NSO)]$, or $[Fe(PPh_3)_2(CNMe)(CO)(4\text{-}NO_2C_6H_4NSO)]$, but CO displaces the ArNSO ligand. Compounds of type I fail to react with MeI or $MeSO_3F$, but with other electrophiles such as $[4\text{-}FC_6H_4N_2]^+$ salts, tetracyanoethylene, or acetic acid, they suffer ArNSO loss with formation of, e.g., $[Fe(PPh_3)_2(CO)_2(NNC_6H_4F\text{-}4)]BF_4$, $[Fe(PPh_3)_2(CO)_2(C_4(CN)_4)]$ with trans CO ligands, and $[Fe(PPh_3)_2(CO)_2(O_2CMe)_2]$ with cis CO groups. The IR spectra of I have been investigated and absorption bands due to their ν(CO), ν(NS), and ν(SO) vibrations identified and assigned. ArNSO are very powerful electron-withdrawing ligands which thus form stable bonds only with relatively electron-rich metal centers. Metal-to-ligand back-donation appears to be an important, perhaps overwhelming, component of the Fe–ArNSO bond which, it is tentatively concluded, is of the η^2-(NS) rather than the η^1-(S) type. The N and S atoms probably lie in the equatorial plane of a trigonally bipyramidally coordinated iron atom while the R_3P ligands occupy the apical coordination positions. The η^1-(S)- and η^2-(NS)-ArNSO–metal bonding are outlined in a qualitative fashion, and the reasons for the relative importance of the second as compared with η^2-(SO)-SO_2 coordination are discussed.

We have shown previously that the sulfur dioxide complexes $[Fe(PR_3)_2(CO)_2(SO_2)]$ (PR_3 is a phosphine or phosphite ligand) exist in solution as mixtures of the two isomers illustrated in Figure 1.[1] In both there is trigonal-bipyramidal coordination about the metal atom with the SO_2 ligand in an equatorial position η^1 bonded via S to Fe with the $FeSO_2$ plane approximately perpendicular to the equatorial plane. In a continuation of this work, we have investigated the preparation, reactions, and IR spectra of the related Fe(0) complexes in which sulfur dioxide has been replaced by sulfinylanilines ArNSO where Ar is a 4-substituted phenyl group.

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Table I. Yields, Melting Points, Analyses, and IR Spectra of Some [Fe(PR$_3$)$_2$(CO)$_2$(ArNSO)] Complexes Described in the Text

				analyses[a]				IR spectra[b]			
Ar	R$_3$P	yield, %	mp, °C	% C	% H	% N	% S	ν(CO)[c]	ν(CO)[c]	ν(SO)[d]	ν(NS)[d]
4-MeOC$_6$H$_4$	Ph$_3$P	30	124-126	66.8 (67.1)	4.9 (4.6)	1.6 (1.7)	4.4 (4.0)	1915 (10)	1975 (6.4)	1059	940
4-MeC$_6$H$_4$	Ph$_3$P	32	92-94	68.4 (68.4)	5.0 (4.7)	1.6 (1.8)	4.3 (4.1)	1915 (10)	1979 (8.0)	1068	952
4-FC$_6$H$_4$	Ph$_3$P	32	123-124	66.6 (66.6)	4.6 (4.3)	1.6 (1.8)	4.2 (4.0)	1917 (10)	1981 (7.1)	1062	951
C$_6$H$_5$	Ph$_3$P	36	108-110	67.8 (68.1)	4.7 (4.5)	1.6 (1.8)	4.4 (4.1)	1918 (10)	1980 (7.3)	1063	950
4-ClC$_6$H$_4$	Ph$_3$P	40	110-112	64.6 (65.0)	4.5 (4.2)	1.6 (1.7)	4.0 (3.9)	1920 (10)	1982 (6.7)	1066	953
4-BrC$_6$H$_4$	Ph$_3$P	43	108-110	61.7 (61.8)	4.2 (4.0)	1.5 (1.6)		1921 (10)	1983 (6.7)	1062	950
4-NO$_2$C$_6$H$_4$	Ph$_3$P	45	141-143	64.0 (64.4)	4.4 (4.1)	3.7 (3.4)	4.2 (3.9)	1931 (10)	1992 (6.5)	1063	938
4-NO$_2$C$_6$H$_4$	(4-MeOC$_6$H$_4$)Ph$_2$P	49	120-123	60.8 (61.2)	4.9 (4.5)	2.9 (3.0)	3.7 (3.4)	1930 (10)	1992 (6.4)	1063	934
4-NO$_2$C$_6$H$_4$	(4-MeOC$_6$H$_4$)$_3$P	44	121-124	60.3 (60.2)	4.5 (4.6)	3.0 (3.2)	3.2 (3.2)	1927 (10)	1992 (6.2)	1059	935
4-NO$_2$C$_6$H$_4$	(4-MeC$_6$H$_4$)Ph$_2$P[e]	49	130-132	67.4 (67.4)	4.8 (4.7)	3.2 (3.1)	3.2 (3.5)	1931 (10)	1993 (6.6)	1062	937
4-NO$_2$C$_6$H$_4$	(4-MeC$_6$H$_4$)$_3$P	55	146-147	66.5 (66.4)	5.1 (5.1)	2.8 (3.1)	4.0 (3.6)	1931 (10)	1993 (6.9)	1066	937
4-NO$_2$C$_6$H$_4$	(4-ClC$_6$H$_4$)$_3$P	46	168-170	51.5 (51.4)	2.7 (2.7)	2.6 (2.7)	3.4 (3.1)	1933 (10)	1993 (7.8)	1074	939
4-NO$_2$C$_6$H$_4$	(PhCH$_2$)$_3$P	39	dec pt 115	66.2 (66.4)	5.2 (5.1)	2.9 (3.1)		1941 (10)	1999 (8.2)	*f*	930
4-ClC$_6$H$_4$	(4-MeC$_6$H$_4$)$_3$P	40	dec pt 124	66.7 (67.2)	5.5 (5.2)	1.6 (1.6)	4.4 (3.6)	1915 (10)	1979 (6.8)	1062	941
4-BrC$_6$H$_4$	(4-MeC$_6$H$_4$)$_3$P	43	dec pt 120	63.6 (63.9)	5.2 (4.9)	1.6 (1.5)	3.6 (3.4)	1917 (10)	1980 (6.6)	1063	938

[a] Found, with calculated values in parentheses. [b] Peak positions (cm^{-1}) with relative peak heights in parentheses. [c] Measured in CHCl$_3$ solution. Similar values obtained by using solid samples. [d] Measured in CsBr disks. [e] Contains C$_6$H$_6$ of crystallization. [f] Cannot be identified with certainty.

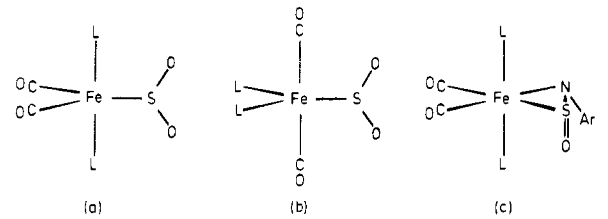

Figure 1. Structures of (a, b) the two isomers of [Fe(L)$_2$(CO)$_2$(η^1-(S)-SO$_2$)] and (c) [Fe(L)$_2$(CO)$_2$(η^2-(NS)-ArNSO)] complexes (L = R$_3$P).

The following sulfinylaniline complexes have been reported: [Pt(PPh$_3$)$_2$(ArNSO)],[2,3] [Ni(PPh$_3$)$_2$(ArNSO)],[4] [RhCl(PR$_3$)$_2$(ArNSO)],[5] [IrCl(PR$_3$)$_2$(ArNSO)] (R = alkyl or aryl, Ar = aryl),[5] and [IrCl(PPh$_3$)$_2$(CO)(4-NO$_2$C$_6$H$_4$NSO)].[2] On the basis of spectroscopic data it was suggested that in the derivatives of Ni(0) and Pt(0) the ArNSO ligands were side-on bonded to the metal via the N–S π bond, η^2-(NS) coordination.[2-4] This was confirmed by an X-ray diffraction study on [Pt(PPh$_3$)$_2$(2,4,6-Me$_3$C$_6$H$_2$NSO)], which also showed that the NSO and P$_2$Pt planes lay at ca. 90° and that the coordinated ArNSO ligand had a cis conformation about the N–S bond.[3] On the other hand, the trans square-planar [MCl(PR$_3$)$_2$(ArNSO)] complexes [M = Rh(I) and Ir(I)] exist as mixtures of interconverting isomers in solution. In one, the cis ArNSO ligand is η^2-(NS) bonded as described above, but in the other it is η^1 bonded through sulfur so that the RhS(O)NAr plane lies at ca. 60° to the RhCl(PR$_3$)$_2$S plane in [RhCl(P(*i*-Pr)$_3$)$_2$(4-MeC$_6$H$_4$NSO)]. The relative importance of these isomers in solution is affected by temperature, by steric and electronic effects within both PR$_3$ and ArNSO ligands, and by M.[5] In the 1:1 adduct of Vaska's compound, [IrCl(PPh$_3$)$_2$(CO)(4-NO$_2$C$_6$H$_4$NSO)], the sulfinylaniline is thought to be η^1-(S) bonded in the apical coordination position of a trans square-based-pyramidal molecule; cf. [IrCl(PPh$_3$)$_2$(CO)(SO$_2$)].[2]

It has been reported that the reactions of [Fe$_2$(CO)$_9$] with ArNSO result in ligand fragmentation. Thus with PhNSO in benzene at 45 °C a low yield of [Fe$_2$(CO)$_6$(PhNS)] was obtained,[6] while PhNHNSO gave PhSH and [Fe$_2$(CO)$_6$(μ-SPh)$_2$].[7]

Experimental Section

Published procedures were used to prepare R$_3$P,[8] MeC(CH$_2$O)$_3$P,[9] MeNC,[10] EtNC,[10] C$_6$H$_{11}$NC,[11] PhCH$_2$NC,[11] and ArNSO ligands[12] and [4-FC$_6$H$_4$N$_2$]BF$_4$,[13] [Fe$_2$(CO)$_9$],[14] [Fe(benzylideneacetone)(CO)$_3$],[15] and [Fe(PPh$_3$)$_3$(CO)$_2$].[16] Other chemicals were purchased.

Unless it is stated otherwise, all reactions were carried out under an atmosphere of purified nitrogen with use of purified solvents. Tetrahydrofuran (THF) was dried and deoxygenated by heating it with sodium and benzophenone and distilling it prior to use. Photochemical reactions were carried out with use of a Philips HPR 125-W lamp.

Infrared spectra were run on a Perkin-Elmer 337 spectrometer equipped with a Hitachi Perkin-Elmer readout recorder. They were calibrated[17] with gaseous DCl–H$_2$O so that peak positions are accurate to within ±2 cm^{-1} in the 1700–2150-cm^{-1} region. The remaining regions of the IR spectrum were investigated by using a Perkin-Elmer 283 B spectrometer with the samples dispersed in CsBr disks. The spectra were calibrated with polystyrene[17] so that their peak positions are only accurate to within ±4 cm^{-1}. They are summarized in Tables I and II.

^{1}H NMR spectra were run on a Perkin-Elmer R12 spectrometer. They were often difficult to obtain because of low sample solubility, and as they gave no useful information, they are not included here.

Mass spectra were measured on a VG 70-70M mass spectrometer. They showed only fragments derived from the free ligands and none derived from the [Fe(PR$_3$)$_2$(CO)$_2$(ArNSO)] molecules. They will not be mentioned again.

Reaction of [Fe$_2$(CO)$_9$] with 4-NO$_2$C$_6$H$_4$NSO. A mixture of [Fe$_2$(CO)$_9$] (0.36 g, 1 mmol and 4-NO$_2$C$_6$H$_4$NSO (0.1 mmol) in THF (25 mL) was stirred. [Fe$_2$(CO)$_9$] dissolved slowly to give a bright red solution, from which a red oil could be isolated by removal of the solvent at reduced pressure. Its IR spectrum showed ν(CO) = 1982 (9.9), 2008 (10), and 2038 (9.2) cm^{-1} (CHCl$_3$ solution with relative peak heights in parentheses). We were unable to purify it further. Other ArNSO species react similarly.

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Table II. Melting Points, Analyses, and IR Spectra of Substituted Derivatives of the $[Fe(PPh_3)_2(CO)_2(ArNSO)]$ Complexes

			analyses[a]				IR spectra[b]			
Ar	L	mp, °C	% C	% H	% N	% S	ν(CO)[c]	ν(CO)[c]	ν(SO)[d]	ν(NS)[d]
			$[Fe(PPh_3)(L)(CO)_2(ArNSO)]$							
$4\text{-}MeC_6H_4$	$MeC(CH_2O)_3P$	dec pt 72	55.5 (55.6)	4.6 (4.5)	2.1 (2.0)	4.1 (4.6)	1948 (10)	2003 (8.7)		
C_6H_5	$MeC(CH_2O)_3P$	dec pt 101	55.8 (56.3)	4.6 (4.5)	2.1 (2.1)	5.4 (4.8)	1950 (10)	2006 (8.1)		
$4\text{-}ClC_6H_4$	$MeC(CH_2O)_3P$	114–116	54.2 (53.5)	4.3 (4.0)	2.0 (2.0)	4.8 (4.6)	1952 (10)	2008 (8.8)		
$4\text{-}BrC_6H_4$	$MeC(CH_2O)_3P$	dec pt 128	49.4 (51.4)	4.2 (3.9)	2.2 (1.9)	4.3 (4.5)	1952 (10)	2008 (8.6)	1020	925
$4\text{-}NO_2C_6H_4$	$MeC(CH_2O)_3P$	134–135	52.2 (52.7)	4.2 (4.0)	3.6 (3.9)	4.4 (4.5)	1964 (10)	2020 (6.6)	1020	929
			$[Fe(L)_2(CO)_2(ArNSO)]$							
$4\text{-}NO_2C_6H_4NSO$	$(MeO)_3P$	115–118	31.1 (30.9)	4.1 (4.0)	5.4 (5.1)	6.1 (5.8)	1965 (10)	2022 (9.4)		
$4\text{-}NO_2C_6H_4NSO$	$(EtO)_3P$	95–97	38.3 (38.2)	5.3 (5.4)	4.3 (4.4)	4.7 (5.1)	1958 (10)	2019 (6.0)		
$4\text{-}NO_2C_6H_4NSO$	$(i\text{-}PrO)_3P$	75–77	43.8 (43.8)	6.4 (6.5)	3.9 (3.9)	4.9 (4.5)	1955 (10)	2017 (7.0)		
$4\text{-}NO_2C_6H_4NSO$	$Me(CH_2O)_3P$	dec pt 150					1972 (10)	2023 (7.0)		
			$[Fe(PPh_3)_2(L)(CO)(ArNSO)]$							
$4\text{-}NO_2C_6H_4NSO$	MeNC	62–64	64.8 (61.2)	4.4 (4.4)	4.8 (5.0)	4.2 (3.8)	1927 (10)	2157 (4.5)[e]	1039	930
$4\text{-}NO_2C_6H_4NSO$	EtNC	dec pt 126	64.8 (65.2)	4.8 (4.6)	4.7 (5.0)	3.8 (3.8)	1925 (10)	2146 (6.2)[e]	1039	929
$4\text{-}NO_2C_6H_4NSO$	$C_6H_{11}NC$	101–103	66.9 (66.6)	5.0 (5.0)	4.5 (4.7)	4.1 (3.6)	1925 (10)	2137 (4.5)[e]	1039	927
$4\text{-}NO_2C_6H_4NSO$	$PhCH_2NC$	dec pt 132	67.1 (67.3)	4.3 (4.5)	4.4 (4.6)	3.7 (3.5)	1929 (10)	2137 (5.0)[e]	1045	933

[a] Found, with calculated values in parentheses. [b] Peak positions (cm^{-1}) with relative peak heights in parentheses. [c] Measured in $CHCl_3$ solution. Similar results obtained by using solid samples. [d] Measured in CsBr disks. Absorption bands due to phosphite ligands obscure this region very badly. [e] Due to ν(CN) of the R′NC ligand.

Reaction of $[Fe_2(CO)_9]$ with ArNSO and PR_3. Mixtures of $[Fe_2(CO)_9]$ (1 g), ArNSO, and R_3P (mole ratio 1:1:2) in THF (50 mL) were stirred until all of the $[Fe_2(CO)_9]$ had dissolved (1–4 h depending primarily on Ar) [R_3P = $(4\text{-}MeOC_6H_4)_3P$, $(4\text{-}MeC_6H_4)_3P$, $(4\text{-}MeOC_6H_4)Ph_2P$, $(4\text{-}MeC_6H_4)Ph_2P$, Ph_3P, or $(4\text{-}ClC_6H_4)_3P$; Ar = $4\text{-}MeOC_6H_4$, $4\text{-}MeC_6H_4$, Ph, $4\text{-}FC_6H_4$, $4\text{-}ClC_6H_4$, $4\text{-}BrC_6H_4$, or $4\text{-}NO_2C_6H_4$]. In most cases the red-brown products were insoluble and precipitated from the reaction mixtures. They were filtered off and recrystallized from ether–methanol or dichloromethane–hexane mixtures. However, the derivatives of PhNSO, $4\text{-}MeC_6H_4NSO$, and $4\text{-}MeOC_6H_4NSO$ were soluble in the reaction mixture so they were isolated by removal of the solvents at reduced pressure and purified by column chromatography (CH_2Cl_2 and alumina) and recrystallization from dichloromethane–hexane mixtures. The reaction yields quoted in Table I refer to this reaction. This table also includes melting point and analytical data for these compounds.

Reaction of [Fe(benzylideneacetone)$(CO)_3$] with $4\text{-}NO_2C_6H_4NSO$ and Ph_3P. A mixture of [Fe(benzylideneacetone)$(CO)_3$] (1 g), $4\text{-}NO_2C_6H_4NSO$, and Ph_3P (mole ratio 1:1:2) in THF (50 mL) was stirred for 2 h. $[Fe(PPh_3)_2(CO)_2(4\text{-}NO_2C_6H_4NSO)]$ precipitated and was purified as described above (yield 73%).

Reaction of $[Fe(PPh_3)_3(CO)_2]$ with ArNSO. Equimolar amounts of $[Fe(PPh_3)_3(CO)_2]$ (1 g) and ArNSO (Ar = Ph or $4\text{-}NO_2C_6H_4$) in THF (50 mL) were stirred for 2 h. The $[Fe(PPh_3)_2(CO)_2(ArNSO)]$ products were isolated and purified as described above (yields ca. 75% in both cases).

Reaction of $[Fe(CO)_5]$ with $4\text{-}NO_2C_6H_4NSO$ and PR_3. A solution of $[Fe(CO)_5]$ (1 mL), $4\text{-}NO_2C_6H_4NSO$, and PR_3 (mole ratio 1:1:2; R_3P = $(4\text{-}MeC_6H_4)_3P$, Ph_3P, or $(4\text{-}ClC_6H_4)_3P$) in THF (50 mL) were UV irradiated for 3 h. The $[Fe(PR_3)_2(CO)_2(4\text{-}NO_2C_6H_4NSO)]$ products were isolated and purified as described above (yields ca. 30%).

Under the same conditions, or on heating, $[Fe(PR_3)_2(CO)_3]$ and $[Fe(PR_3)(CO)_4]$ failed to react with $4\text{-}NO_2C_6H_4NSO$.

Reaction of $[Fe(PPh_3)_2(CO)_2(ArNSO)]$ with $P(OR)_3$. A solution of $[Fe(PPh_3)_2(CO)_2(ArNSO)]$ (1 g) and $(RO)_3P$ (Ar = $4\text{-}MeOC_6H_4$, Ph, $4\text{-}ClC_6H_4$, $4\text{-}BrC_6H_4$, or $4\text{-}NO_2C_6H_4$; $(RO)_3P$ = $(MeO)_3P$, $(EtO)_3P$, $(i\text{-}PrO)_3P$, or $MeC(CH_2O)_3P$) in benzene (50 mL) was stirred. With a reactant mole ratio of 1:1, a reaction to give $[Fe(PPh_3)(P(OR)_3)(CO)_2(ArNSO)]$ was completed within 5 min. Then the reaction mixtures were filtered, the solvents removed at reduced pressures, and the red oils thus obtained crystallized from THF–methanol or ether–hexane mixtures. Unfortunately only those products for which $(RO)_3P$ = $MeC(CH_2O)_3P$ gave satisfactory analyses, and they are included in Table II. These reactions are virtually quantitative.

With a reactant mole ratio of 1:2 and reaction times of 30 min, $[Fe(P(OR)_3)_2(CO)_2(ArNSO)]$ complexes were obtained. The products were isolated and purified as before. When $(RO)_3P$ = $MeC(CH_2O)_3P$, the products were too insoluble to be purified by recrystallization, while for the other $(RO)_3P$ complexes only those with ArNSO = $4\text{-}NO_2C_6H_4NSO$ would crystallize and are included in Table II. Reaction yields again were very high (>90%).

Reaction of $[Fe(PPh_3)_2(CO)_2(4\text{-}NO_2C_6H_4NSO)]$ with R′NC. A solution of $[Fe(PPh_3)_2CO)_2(4\text{-}NO_2C_6H_4NSO)]$ (0.5 g) and R′NC (mole ratio 1:1; R′ = Me, Et, cyclo-C_6H_{11}, or $PhCH_2$) in benzene (40 mL) was stirred for 6–8 h. When the reaction was complete, the solvent was removed at reduced pressure and the residue recrystallized from dichloromethane–hexane mixtures to give $[Fe(PPh_3)_2(CNR')(CO)(4\text{-}NO_2C_6H_4NSO)]$. The reactions appeared to be virtually quantitative, but the yields of purified products were much lower at 40–50%.

If a large excess of R′NC was used, non-CO-containing species were formed, but they could not be identified.

Reaction of $[Fe(PPh_3)_2(CO)_2(4\text{-}ClC_6H_4NSO)]$ with CO. CO gas was bubbled through a solution of $[Fe(PPh_3)_2(CO)_2(4\text{-}ClC_6H_4NSO)]$ (1 g) in benzene (50 mL) in the dark and in the prevailing laboratory light. In both instances $[Fe(PPh_3)(CO)_4]$ was the major product, but a little $[Fe(PPh_3)_2(CO)_3]$ was also formed. Similar behavior was exhibited by complexes of other ArNSO ligands, but no attempts were made to isolate the products.

Reaction of $[Fe(PPh_3)_2(CO)_2(4\text{-}NO_2C_6H_4NSO)]$ with Ph_2C_2. Equimolar amounts of the reagents in benzene solution at 60 °C failed to react even after 4 h.

Reaction of $[Fe(PPh_3)_2(CO)_2(4\text{-}NO_2C_6H_4NSO)]$ with CS_2. When $[Fe(PPh_3)_2(CO)_2(4\text{-}NO_2C_6H_4NSO)]$ (0.5 g) was dissolved in CS_2 (50 mL), it underwent a slow reaction. The only product isolated after 4 h was $[Fe(PPh_3)_2(CO)_3]$ identified by IR spectroscopy and analysis (yield ca. 50%).

Reaction of $[Fe(PPh_3)_2(CO)_2(ArNSO)]$ with MeI, EtI, or $MeSO_3F$. No reaction took place between $[Fe(PPh_3)_2(CO)_2(ArNSO)]$ (Ar = Ph or $4\text{-}BrC_6H_4$) and MeI, EtI, or $MeSO_3F$ in benzene solution even with very high reactant mole ratios (up to 1:10), long reaction times (up to 24 h), or elevated temperatures (50 °C for $MeSO_3F$).

Reactions of $[Fe(PPh_3)_2(CO)(L)(ArNSO)]$ with $[4\text{-}FC_6H_4N_2]BF_4$. To a solution of $[Fe(PPh_3)_2(CO)(L)(ArNSO)]$ (0.5 g) (Ar = Ph and L = CO; Ar = $4\text{-}NO_2C_6H_4$ and L = $PhCH_2NC$) in benzene (40 mL) was added a solution of $[4\text{-}FC_6H_4N_2]BF_4$ (reactant mole ratio 1:1) in acetone (5 mL) over a period of 30 min. $[Fe(PPh_3)_2(CO)_2(NNC_6H_4F\text{-}4)]BF_4$ precipitated as an orange solid, which was filtered off, washed with benzene, and dried: yield 95%; mp 209–211 °C; IR ν(CO) 1977 (10) and 2027 (6.8) cm^{-1}, ν(NN) 1712 (4.6, br) cm^{-1} (in $CHCl_3$ solution with relative peak heights in parentheses). Anal. Calcd: C, 62.4; H, 4.0; N, 3.3; S, 0; F, 11.2. Found: C, 62.0; H, 3.7; N, 3.1; S, 0; F, 10.8. $[Fe(PPh_3)_2(CO)(CNCH_2Ph)(NNC_6H_4F\text{-}4)]BF_4$ was isolated by removal of the solvent at room temperature and recrystallized from methanol: yield 82%; dec pt 134 °C; IR ν(CN) 2060 cm^{-1}, ν(CO) 1951 cm^{-1}, ν(NN) 1720 cm^{-1} (in $CHCl_3$ solution). Anal. Calcd: C, 65.4; H, 4.4; N, 4.5; S, 0; F, 10.2. Found: C, 65.0; H, 4.1; N, 4.2; S, 0; F, 9.6.

Reaction of $[Fe(PPh_3)_2(CO)_2(PhNSO)]$ with $C_2(CN)_4$. To a solution of $[Fe(PPh_3)_2(CO)_2(PhNSO)]$ (0.5 g) in toluene (50 mL) was added $C_2(CN)_4$ (mole ratio 1:1). The color of the reaction mixture changed immediately from red to green. After 4 h the solvent was removed partially with deposition of yellow crystals of $[Fe(PPh_3)_2(CO)_2(C_2(CN)_4)]$, which were dried: yield 54%; mp 60 °C dec; IR ν(CO) 1982 cm^{-1} and ν(CN) 2222 cm^{-1} (in $CHCl_3$ solution). Anal. Calcd: C, 69.1; H, 3.9; N, 7.3; S, 0. Found: C, 68.5; H, 4.1; N, 6.9; S, 0.

Reaction of $[Fe(PPh_3)_2(CO)_2(PhNSO)]$ with Acetic Acid. $[Fe(PPh_3)_2(CO)_2(PhNSO)]$ (1 g was dissolved in benzene (40 mL) and glacial acetic acid (2 mL) added. The red solution turned yellow immediately. After 2 h it was filtered, methanol (10 mL) added, and the whole cooled. Yellow crystals of $[Fe(PPh_3)_2(CO)_2(O_2CMe)_2]$ were deposited: yield 35%; mp 105–106 °C; IR ν(CO) 1978 (10) and 2029 (9.7) cm^{-1} (in $CHCl_3$ with relative peak heights in parentheses). Anal. Calcd: C, 66.8; H, 4.8; N, 0; S, 0. Found: C, 67.0; H, 4.9; N, 0; S, 0.

Results and Discussion

The slow reactions of sulfinylanilines ArNSO with $[Fe_2(CO)_9]$ in tetrahydrofuran (THF) solution at room temperature give $[Fe(CO)_5]$ (identified by IR spectroscopy) and red oils. These could not be identified unambiguously, but with PPh_3 they are converted to $[Fe(PPh_3)_2(CO)_2(ArNSO)]$ with evolution of CO gas. Consequently, it is possible that they are $[Fe(CO)_4(ArNSO)]$ derivatives formed from $[Fe_2(CO)_9]$ via $[Fe(CO)_4(THF)]$ (cf. ref 18). If our proposal is correct, then ArNSO and SO_2[19] give different types of products in their reactions with $[Fe_2(CO)_9]$ despite their close formula and structural relationships. Identical reactions carried out in benzene solution were less clear-cut and were not investigated further.

Our most widely utilized route to the $[Fe(PR_3)_2(CO)_2(ArNSO)]$ complexes (I) listed in Table I was the reaction of $[Fe_2(CO)_9]$ with ArNSO and R_3P in THF solution at room temperature. $[Fe(CO)_5]$ (II) was also formed together with varying amounts of mainly $[Fe(PR_3)(CO)_4]$ (III) and some $[Fe(PR_3)_2(CO)_3]$ (IV). The product ratios depend on both ArNSO and R_3P. The yields of I increase and those of III and IV decrease (to zero when Ar = $4\text{-}NO_2C_6H_4$) along the series Ar = $4\text{-}MeOC_6H_4 < 4\text{-}MeC_6H_4 < 4\text{-}FC_6H_4 < C_6H_5 < 4\text{-}ClC_6H_4 < 4\text{-}BrC_6H_4 < 4\text{-}NO_2C_6H_4$ when $R_3P = Ph_3P$, paralleling closely the increase in overall electron-withdrawing ability of the para substituent on the phenyl groups as measured by the Taft σ_p constant.[20] The reaction times decrease along the same series. This is not surprising as the more rapid is the rate of formation of I the lower will be the proportion of $[Fe_2(CO)_9]$ or $[Fe(CO)_4(THF)]$ that will be converted to other compounds, notably III and IV. If trialkyl or triphenyl phosphites are used in place of triarylphosphines for R_3P, no I may be isolated. Only III with some IV appears to be formed. This may be because the competing reactions of $[Fe(CO)_4(THF)]$ with R_3P are much faster when R is an alkoxy or phenoxy group than when it is aryl or benzyl. In no reaction did we observe significant amounts of products arising from breakdown of the ArNSO ligand.

If the reaction proceeds solely via breakdown of $[Fe_2(CO)_9]$ to inert $[Fe(CO)_5]$ and reactive $[Fe(CO)_4(THF)]$, a maximum of 50% of the iron can be converted to I. This is found to be the case in all instances except those where ArNSO = $4\text{-}NO_2C_6H_4NSO$. Then yields may reach 55% (Table I). This surplus could only arise from $[Fe(CO)_5]$, which undergoes a photochemical reaction with Ph_3P and $4\text{-}NO_2C_6H_4NSO$ to give $[Fe(PPh_3)_2(CO)_2(4\text{-}NO_2C_6H_4NSO)]$ (31% yield), III, and IV. These last two compounds appear to be inert to the replacement of CO by $4\text{-}NO_2C_6H_4NSO$ in either thermal or photochemical reactions.

High yields of I may be obtained from the reactions of ArNSO either with $[Fe(PPh_3)_3(CO)_2]$ or with [(benzylideneacetone)$Fe(CO)_3$] and Ph_3P. These methods were not utilized extensively.

The $[Fe(PR_3)_2(CO)_2(ArNSO)]$ complexes are brown to red microcrystalline solids, which would not give larger crystals despite our efforts to obtain them. They are insoluble in water, soluble to some extent in most organic solvents, and reasonably stable in air. Increasing the electron-withdrawing ability of Ar in the ArNSO ligand increases the intensity of the red color of I, decreases their solubility in organic solvents, and increases their air stability. Thus the $4\text{-}NO_2C_6H_4NSO$ derivatives are sparingly soluble crimson solids that are unaffected by air even after 3 years. On the other hand, the $4\text{-}MeOC_6H_4NSO$ complexes are red-brown soluble solids that show evidence of decomposition by air after a few weeks.

Reactions with Nucleophiles and Electrophiles. The Ph_3P ligands of the $[Fe(PPh_3)_2(CO)_2(ArNSO)]$ complexes are labile, as they are in $[Fe(PPh_3)_2(CO)_2(\eta^2\text{-}CS_2)]$[21] and $[Fe(PPh_3)_2(CO)_2(\eta^1\text{-}SO_2)]$ derivatives. Those where Ar = $4\text{-}BrC_6H_4$ or $4\text{-}NO_2C_6H_4$ react with $(PhO)_3P$ to give an equilibrium mixture with a second species, ν(CO) = ca. 1933 and 1995 cm^{-1}, which could not be isolated. However, with other phosphites L = $(MeO)_3P$, $(EtO)_3P$, $(i\text{-}PrO)_3P$, or $MeC(CH_2O)_3P$, rapid and complete Ph_3P displacement took place to give (a) $[Fe(PPh_3)(L)(CO)_2(ArNSO)]$ after ca. 5 min with a reactant mole ratio of 1:1 and then (b) $[Fe(L)_2(CO)_2(ArNSO)]$ after ca. 30 min with a reactant mole ratio of 1:2. Only the products listed in Table II could be obtained in a pure state, but the others were identified by IR spectroscopy.

The reactions between $[Fe(PPh_3)_2(CO)_2(4\text{-}NO_2C_6H_4NSO)]$ and R′NC (R′ = Me, Et, C_6H_{11}, or $PhCH_2$) are not straightforward. Although the final products, $[Fe(PPh_3)_2(CNR')(CO)(4\text{-}NO_2C_6H_4NSO)]$, are those resulting from CO displacement, spectroscopic studies show that the first step is displacement of Ph_3P by R′NC, and the liberated Ph_3P then displaces CO. If the free Ph_3P is trapped by reaction with a KI–$CuCl_2$ mixture, the second step of the reaction does not take place. An orange solid precipitated when RNC = EtNC. It, like the intermediate species in the reaction solution, shows ν(CO) 1956 (10) and 2009 (6.3) cm^{-1} and ν(CN) 2164 (6.8) cm^{-1} ($CHCl_3$ solution with relative peak heights in parentheses). Unfortunately consistent analyses could not be obtained for it, but it may be $[Fe(PPh_3)(CNEt)(CO)_2(4\text{-}NO_2C_6H_4NSO)]$.

Unlike the nucleophiles discussed above, CO reacts with $[Fe(PPh_3)_2(CO)_2(4\text{-}ClC_6H_4NSO)]$ either in the dark or in normal laboratory light by displacing the sulfinylaniline. The principal product was $[Fe(PPh_3)(CO)_4]$, but some $[Fe(PPh_3)_2(CO)_3]$ was also formed. The implications of this will be discussed below.

Although $[Fe(PPh_3)_2(CO)_2(4\text{-}NO_2C_6H_4NSO)]$ fails to react with Ph_2C_2 (cf. $[Fe(PR_3)_2(CO)_2(\eta^2\text{-}CS_2)]$ and $C_2(CO_2Me)_2$[22]), with CS_2 it gave $[Fe(PPh_3)_2(CO)_3]$ as the only isolable product. IR spectroscopic monitoring shows the reaction to be complicated. Similarly, CS_2 will displace SO_2 from $[Pt(PPh_3)_2(\eta^1\text{-}SO_2)]$ to give $[Pt(PPh_3)_2(\eta^2\text{-}CS_2)]$. In contrast, SO_2 will displace CS_2 from $[Fe(PPh_3)_2(CO)_2(\eta^2\text{-}CS_2)]$ (forming $[Fe(PPh_3)_2(CO)_2(\eta^1\text{-}SO_2)]$) but ArNSO species do not react with it.

Although the alkylating agents MeI, EtI, or $MeSO_3F$ fail to react with a variety of $[Fe(PR_3)_2(CO)(L)(ArNSO)]$ com-

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plexes (L = CO or R′NC), other electrophiles replace the sulfinylaniline. Thus, from the appropriate substrates, [4-F-$C_6H_4N_2$]BF_4 gives [Fe(PR_3)$_2$(CO)(L)($N_2C_6H_4$F-4)]BF_4 salts, acetic acid forms the octahedral iron(II) complex [Fe(PPh_3)$_2$(CO)$_2$(OAc)$_2$], and tetracyanoethylene (TCNE) gives [Fe(PPh_3)$_2$(CO)$_2$(TCNE)]. In the acetato derivative the two CO groups are mutually cis while steric effects would be expected to cause the Ph_3P ligands to be mutually trans. The TCNE complex, on the other hand, shows only a single IR absorption band due to its ν(CO) vibrations so that the two CO groups must be mutually trans and the Ph_3P ligands mutually cis (cf. [Fe(P(OPh)$_3$)$_2$(CO)$_2$(TCNE)] in ref 23).

In many of their reactions with both electrophiles and nucleophiles, the [Fe(PR_3)$_2$(CO)$_2$(ArNSO)] complexes resemble their [Fe(PR_3)$_2$(CO)$_2$(η^1-SO_2)] and [Fe(PR_3)$_2$(CO)$_2$(η^2-CS_2)] counterparts. In particular, CO is the only nucleophile that displaces the ArNSO or CS_2 ligands from their complexes. By analogy with arguments presented elsewhere for the CS_2 systems,[21] it seems reasonable to suggest that CO, like other nucleophiles, initially displaces phosphines from [Fe(PR_3)$_2$(CO)$_2$(ArNSO)]. However, in the resultant [Fe(PR_3)(CO)$_3$(ArNSO)] the ArNSO ligands are very labile and readily displaced by CO or free PR_3. As for CS_2, this behavior suggests that ArNSO are very powerful electron-withdrawing ligands that only form stable complexes with comparatively electron-rich metal centers. These conclusions are also consistent with the spectroscopic data discussed below.

IR Spectra and Structure. The IR spectra of the [Fe(PR_3)$_2$(CO)$_2$(ArNSO)] complexes (Tables I and II) show two absorption bands between 1800 and 2100 cm^{-1}. The broader and stronger bands at lower frequencies (1910–1940 cm^{-1}) are assigned to the asymmetric ν(CO) vibrations of the Fe(CO)$_2$ moieties, and the sharper and weaker ones at higher frequencies (1975–1995 cm^{-1}) to the symmetric modes. Their relative intensities are consistent with trigonal-bipyramidal coordination about the Fe atom with the CO groups in equatorial positions. On steric grounds, the R_3P ligands would be expected to occupy both axial positions. The R′NC ligands, presumably, replace one of the equatorial CO groups. The relatively high frequencies of these ν(CO) vibrations, when compared with those of other [Fe(PPh_3)$_2$(CO)$_2$(L)] derivatives, suggest that the overall electron-withdrawing ability of the ArNSO ligands is much greater than that of L = CO [when L = CO, ν(CO) = 1886 and ca. 1959 cm^{-1}, CS_2 solution[24]], less than that of L = [4-$FC_6H_4N_2$]$^+$ [ν(CO) = 1977 and 2027 cm^{-1}, $CHCl_3$ solution], and comparable to that of η^2-CS_2 [ν(CO) = 1930 and 1993 cm^{-1}, CS_2 solution[21]] or η^1-SO_2 [ν(CO) = 1916 and 1974 cm^{-1}, CS_2 solution[1]]. These frequencies vary with PR_3 in the expected manner and with X in Ar = 4-XC_6H_4 so that for R_3P = Ph_3P they increase as X = MeO < Me < F ~ H < Cl ~ Br << NO_2. This series parallels the increasing overall electron-withdrawing ability of X as measured by the Taft σ_p constant.[20] The increasing electron-withdrawing ability of the Ar group obviously increases the Lewis acidity of the ArNSO ligand, and this in turn affects the electron density at the metal atom. These spectroscopic observations are consistent with a very large metal-to-ligand π contribution to the overall ArNSO–Fe bond as was suggested above on the basis of chemical reactivity.

Absorption bands due to the ν(NS) and ν(SO) modes of the coordinated ArNSO ligands would be expected to have frequencies between 900 and 1300 cm^{-1}.[3,5] The IR spectra of [Fe(PPh_3)$_2$(CO)$_2$(ArNSO)] show a plethora of absorption bands in this region, but there are two that are not present in the spectra of [Fe(PPh_3)$_2$(CO)$_3$], free Ph_3P, and free ArNSO where Ar is not Ph or 4-MeC_6H_4. One is of medium intensity at ca. 940 cm^{-1}, and the other is stronger at ca. 1060 cm^{-1}. Their counterparts may be identified in the spectra of other compounds. By reference to the work of Vrieze et al.[3,5] we tentatively suggest that they are due respectively to the ν(NS) and ν(SO) modes of the ArNSO ligands that are η^2 bonded via N and S to the Fe atom. Spectroscopic studies using ^{15}N isotopic labeling have shown that two isomers of [Rh(P(i-Pr)$_3$)$_2$(Cl)(C_6H_5NSO)] coexist in equilibrium in solution.[5] In one where the PhNSO ligand is η^2 bonded via N and S, ν(NS) = 959 and ν(SO) = 1057 cm^{-1}. In the other where the ligand is η^1 bonded through sulfur to the metal atom, ν(NS) = 1269 and ν(SO) = 1108 cm^{-1}.[5] In [Pt(PPh_3)$_2$(PhNSO)] with η^2-(NS) bonding of the cis PhNSO, ν(NS) = 926 and ν(SO) = 1050 cm^{-1}. We are suggesting that [Fe(PR_3)$_2$(CO)$_2$(ArNSO)] complexes do not have structures related to that of [Fe(P(OPh)$_3$)$_2$(CO)$_2$(SO_2)] with its planar η^1-SO_2 ligand.[1] The two alternatives are illustrated in Figure 1. It should be remembered that these conclusions are tentative and based solely on spectroscopic studies in a "crowded" part of the IR spectrum. Unfortunately, we have not been able to grow crystals of our compounds that would be suitable for an X-ray diffraction study.

It is not clear why the ArNSO ligand should (apparently) bond to Fe(0) in an η^2-(NS) fashion while for SO_2 planar η^1-(S) coordination is preferred.[1] It seems unlikely to be a consequence of steric interaction between the Ar group and the axial ligands, which might be possible in the η^1-ArNSO isomer. In part, these would probably be limited if the Ar and O groups maintain the cis conformation about the N–S bond that has been found in [Rh(P(i-Pr)$_3$)$_2$(Cl)(η^1-4-MeC_6H_4NSO)] and in the free ligands,[25] and if they became large they could be reduced by an isomerization similar to that exhibited by [Fe(P(OR)$_3$)$_2$(CO)$_2$(η^1-SO_2)] derivatives.[1] Furthermore, increasing the bulk of the Ar group in [Rh(P(i-Pr)$_3$]$_2$(Cl)(ArNSO)] derivatives increases the importance of the η^1-(S) with respect to the η^2-(NS) isomer. Thus, electronic factors seem to be important. It has been shown that for the [M(PR_3)$_2$(Cl)(ArNSO)] complexes the η^2-(NS) isomers increase and the η^1-(S) decrease in importance in going from M = Ir to M = Rh.

In describing η^2-(NS)-ArNSO–metal bonding, we utilize the scheme suggested by Mingos for a η^2-SO_2 complex[26] and discussed in greater detail by Ryan et al.[27] If the N–S bond lies in the xy plane about the metal atom M, electron donation takes place from the filled metal d_{xy} orbital into the N–S component of the vacant antibonding NSO π^* orbital, which corresponds to the SO_2 π^* orbital $2b_1$. (The bonding and orbital labeling in SO_2 are discussed in detail in ref 28.) As a consequence the N–S–O plane lies approximately perpendicular to the plane of the three-membered M–N–S (cf. ref 3). The filled sulfur "lone-pair" n orbital does not appear to have an important bonding role in this isomer, but the filled N–S π orbital (or the N–S component of a N–S–O π orbital) presumably donates electrons into a vacant metal orbital of the correct symmetry ($d_{x^2-y^2}$, d_{xy}, p_x, p_y, or a combination thereof) that lies in the xy or equatorial plane of the complex. As this π orbital is likely to be of lower energy than the n "lone-pair" orbital, ligand-to-metal electron donation is likely to be limited. This is consistent with the suggestion made above that metal-to-ligand back-donation forms a very (perhaps overwhelmingly) important component in the overall metal–ArNSO bonding. It is worth noting that it is the same filled metal orbital that overlaps with and donates electrons

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into the vacant $2b_1$ acceptor orbital of a SO_2 ligand when it is η^1 bonded through S.[24] As a consequence, the SO_2 plane lies almost perpendicular to the equatorial coordination plane of the Fe atom.

In attempting to explain why the ArNSO ligand show a greater tendency to adopt η^2 as opposed to η^1 coordination than does SO_2, it should be borne in mind that irrespective of the η^1 vs. η^2 balance, η^2-(NS) is markedly preferred over η^2-(SO) in ArNSO complexes despite steric effects favoring the latter (cf. ref 5). It seems likely that in a molecule X═S═O, π bonding would decrease X = O > NAr. (It is consistent with this supposition that MeN–SO, 1.525 (4) Å,[25] is much longer than O–SO, 1.4321 Å,[29] whereas MeNS–O is 1.451 (5) Å[25]). Consequently, there would be an increase in the energy of the filled N–S–O π orbital (the equivalent of $1b_1$ in SO_2), which would have greater oxygen 2p character than nitrogen, and a decrease in the energy of the vacant N–S–O π^* orbital (the equivalent of $2b_1$ in SO_2), which would have greater nitrogen 2p character than oxygen. The former is thus able to compete more effectively with the n orbital as an electron donor, while the latter becomes a better acceptor. If, as proposed above, the Fe–ArNSO bond is largely back-bonding in character, it would be centered on the S–N bond so that η^2-(NS) bonding would be preferred to η^2-(SO) and, in our compounds, to η^1-(S). In other systems, the relative energies of the relevant metal donor and acceptor orbitals will obviously determine which of the bonding alternatives is adopted. Increasing the electron-withdrawing ability of the Ar group will lower the energy of the π^* orbital, increase the back-bonding to the η^2-(NS)-ArNSO ligand from the metal while reducing that to the CO ligands, and consequently lower the ν(CO) frequencies (Table I).

Nature of the $[Fe_2(CO)_9]$–ArNSO Product. We have suggested that the red compound obtained from the reaction of $[Fe_2(CO)_9]$ and various ArNSO species is $[Fe(CO)_4(ArNSO)]$. The presence of three absorption bands due to its IR-active ν(CO) vibrations is consistent with axially substituted trigonal-bipyramidal coordination about the iron atom but does not define it unambiguously. The frequencies of these vibrations are relatively low (for $[Fe(CO)_5$ $\nu(CO) = 1997, 2022, 2031$, and 2114 cm^{-1}) which implies that the ArNSO ligand is acting here as a poorer π acceptor than CO, though better than PPh_3, and therefore cannot be either η^1-(S) or η^2-(NS) bonded. We suggest that it is η^1-(N) bonded via the lone pair on the N atom so that there is a N to Fe σ bond, possibly with some back-bonding into the NSO π^* orbital (the equivalent of the SO_2 $2b_1$ orbital). This mode of bonding has not been observed previously in ArNSO complexes, but it has been reported for the sulfur diimide derivative $[PtCl_2(C_2H_4)(\eta^1$-(N)-*t*-BuNSN-*t*-Bu)].[30]

Registry No. I (Ar = 4-$MeOC_6H_4$, R = Ph), 85134-75-4; I (Ar = 4-MeC_6H_4, R = Ph), 85134-76-5; I (Ar = 4-FC_6H_4, R = Ph), 85134-77-6; I (Ar = C_6H_5, R = Ph), 85134-78-7; I (Ar = 4-ClC_6H_4, R = Ph), 85134-79-8; I (Ar = 4-BrC_6H_4, R = Ph), 85134-80-1; I (Ar = 4-$NO_2C_6H_4$, R = Ph), 85134-81-2; I (Ar = 4-$NO_2C_6H_4$, R = 4-$MeOC_6H_4$), 85134-83-4; I (Ar = 4-$NO_2C_6H_4$, R = 4-MeC_6H_4), 85134-85-6; I (Ar = 4-$NO_2C_6H_4$, R = 4-ClC_6H_4), 85134-86-7; I (Ar = 4-$NO_2C_6H_4$, R = $PhCH_2$), 85134-87-8; I (Ar = 4-ClC_6H_4, R = 4-MeC_6H_4), 85134-88-9; I (Ar = 4-BrC_6H_4, R = 4-MeC_6H_4), 85134-89-0; I (Ar = 4-$NO_2C_6H_4$, R = MeO), 85115-71-5; I (Ar = 4-$NO_2C_6H_4$, R = EtO), 85115-72-6; I (Ar = 4-$NO_2C_6H_4$, R = *i*-PrO), 85134-92-5; II, 13463-40-6; $Fe((4\text{-}MeOC_6H_4)Ph_2P)_2(CO)_2(4\text{-}NO_2C_6H_4NSO)$, 85134-82-3; $Fe((4\text{-}MeC_6H_4)Ph_2P)_2(CO)_2(4\text{-}NO_2C_6H_4NSO)$, 85134-84-5; $[Fe(PPh_3)(MeC(CH_2O)_3P)(CO)_2(4\text{-}MeC_6H_4NSO)]$, 85134-90-3; $[Fe(PPh_3)(MeC(CH_2O)_3P)(CO)_2(PhNSO)]$, 85134-91-4; $[Fe(PPh_3)(MeC(CH_2O)_3P)(CO)_2(4\text{-}ClC_6H_4NSO)]$, 85115-68-0; $[Fe(PPh_3)(MeC(CH_2O)_3P)(CO)_2(4\text{-}BrC_6H_4NSO)]$, 85115-69-1; $[Fe(PPh_3)(MeC(CH_2O)_3P)(CO)_2(4\text{-}NO_2C_6H_4NSO)]$, 85115-70-4; $[Fe(Me(CH_2O)_3P)_2(CO)_2(4\text{-}NO_2C_6H_4NSO)]$, 85115-73-7; $[Fe(PPh_3)_2(MeNC)(CO)(4\text{-}NO_2C_6H_4NSO)]$, 85115-74-8; $[Fe(PPh_3)_2(EtNC)(CO)(4\text{-}NO_2C_6H_4NSO)]$, 85115-75-9; $[Fe(PPh_3)_2(C_6H_{11}NC)(CO)(4\text{-}NO_2C_6H_4NSO)]$, 85115-76-0; $[Fe(PPh_3)_2(PhCH_2NC)(CO)(4\text{-}NO_2C_6H_4NSO)]$, 85115-77-1; $[Fe_2(CO)_9]$, 15321-51-4; $[FeB(CO)_3]$ (B = benzylideneacetone), 38333-35-6; $[Fe(PPh_3)_3(CO)_2]$, 15739-18-1; $[Fe(PPh_3)_2(CO)(CNCH_2Ph)(NNC_6H_4F\text{-}4)]BF_4$, 85097-64-9; $[Fe(PPh_3)_2(CO)_2(C_2(CN)_4)]$, 85097-65-0; $[Fe(PPh_3)_2(CO)_2(O_2CMe)_2]$, 85097-66-1.

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(Vinyloxy)chlorocyclotriphosphazenes

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The reactions of the lithium enolate of acetaldehyde, $LiOCHCH_2$, with hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, lead to the series of (vinyloxy)chlorocyclotriphosphazenes, $N_3P_3Cl_{6-n}(OCH{=}CH_2)_n$ (n = 1–6). Evidence for the occurrence of all possible geometrical and positional isomers in the series has been obtained from the ^{31}P NMR spectra. The principal products are the nongeminal species with comparable amounts of cis and trans isomers being formed. Small amounts of the geminal isomers are also observed. The mono- and pentasubstituted derivatives have been converted to their dimethylamino derivatives, $N_3P_3(OCH{=}CH_2)_{6-n}[N(CH_3)_2]_n$ (n = 1, 5).

Introduction

Although there have been extensive investigations into the reactions of amines[1-3] and more recently of organometallic reagents[4] with cyclophosphazenes, the corresponding reactions with alcohols have received considerably less attention. Detailed studies of the substitution pattern followed in the reactions of phenoxide[5] and the trifluoroethoxide[6] ions with hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, have appeared. Less detailed studies of the reactions of other selected alkoxides with

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